Spinodal in a liquid–solid phase separation

Department of Bioscience and Bioinformatics, Kyushu Institute of Technology
Akihiko Matsuyama [1]

液体相と結晶相の相分離や，液体相から bcc 結晶や fcc 結晶への相転移を記述するためのファン・デア・ワールス型の平均場理論を紹介する。bcc 結晶や fcc 結晶などの結晶構造に対する並進秩序パラメーターを定義することで，液体相からの相転移を議論し，温度と濃度に依存した相分離，スピノダル領域について計算する。液体相ー bcc 結晶相の 2 相分離過程における fcc 構造の不安定性について議論する。

A simple model is introduced to describe liquid-bcc-fcc phase transitions and phase separations, including unstable and metastable regions[1]. We introduce translational order parameters, or degree of a crystalline ordering, for bcc and fcc structures. Combining a van der Waals theory for an imperfect gas with these translational order parameters, we derive the free energy, which is given by one conserved order parameter (concentration) and nonconserved order parameters (degree of a crystalline order). We calculate the phase diagrams on the temperature-concentration plane and find bcc and fcc unstable regions, a bcc-fcc phase separation, and a liquid-bcc-fcc triple point. We also calculate temporal evolution of structure factors for concentration and for crystalline order, depending on a quench temperature and concentration and find a new spinodal decomposition, driven by the instability of a fcc ordering.

1 Results

Figure 1 shows the phase diagram on the reduced-temperature (k_BT/u_0) and concentration (ϕ) plane for $s = 6$ and (a) α=0.125, (b)α=0.0375. The solid curve shows the binodal and the dotted lines show the liquid-bcc phase transition and the bcc-fcc phase transition curve. The liquid-bcc transition line exists at lower concentrations and higher temperatures than the bcc-fcc phase transition line. The dash line is the spinodal curve and the dashed-dotted line shows the liquid spinodal. In the phase diagram, we find a triple point (three-phase coexistence) where the liquid, bcc, and fcc solid phases can simultaneously coexist. At the higher temperature side of the triple point we find the biphasic region, where the liquid phase coexists with the bcc crystalline phase. We also find two-phase coexistence between the bcc and fcc phases at higher

[1]E-mail: matuyama@bio.kyutech.ac.jp

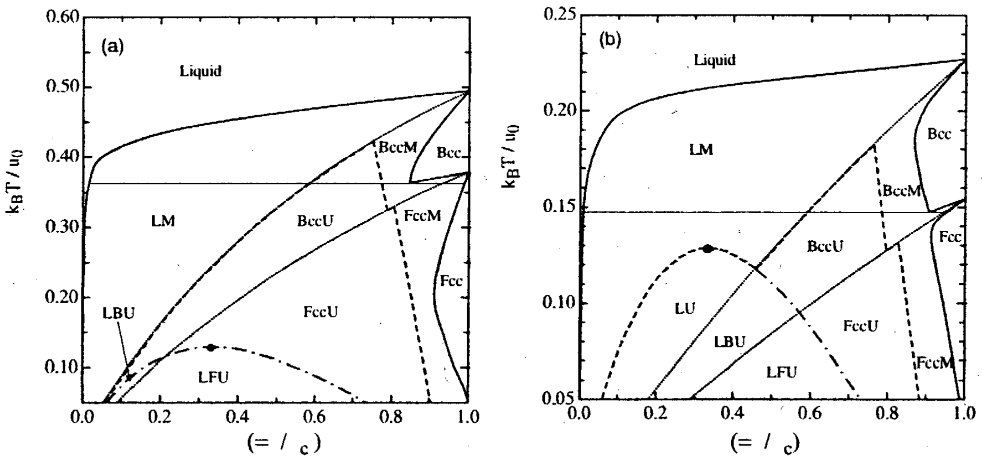

Figure 1: Phase diagram on the reduced-temperature k_BT/u_0 and concentration ϕ plane for $s = 6$ and (a) α=0.125, (b)α=0.0375.

concentrations. At the lower temperature side of the triple point, the broad biphasic region between the liquid and fcc solid phases appears. The liquid-liquid phase separation disappears because the liquid-bcc phase transition line is shifted to higher temperatures.

Inside the spinodal line, corresponding to unstable regions in the free energy, we find five unstable regions. When the system is quenched from a homogeneous liquid phase into these unstable regions, the fluctuations of concentration and that of crystalline structures take place and we can expect a variety of spinodal decompositions even in the early stage. The bcc unstable (BccU) region, lying below the spinodal curve, or the liquid-bcc transition line, and above the bcc-fcc transition line, corresponds to a state that is initially unstable with respect to the order parameter σ_b for the bcc structure but metastable with respect to the concentration and the order parameter σ_f for the fcc structure.

References

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